

SYNTHESIS OF γ -SUBSTITUTED-PROPYLCYCLO-TETRA-SILOXANES AND THEIR EMULSION COPOLYMERIZATION WITH OCTAMETHYL-CYCLOTETRA-SILOXANE*

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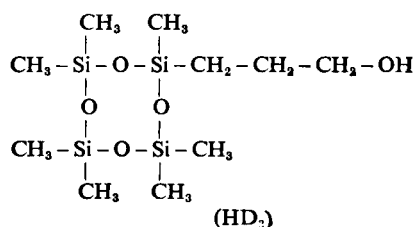
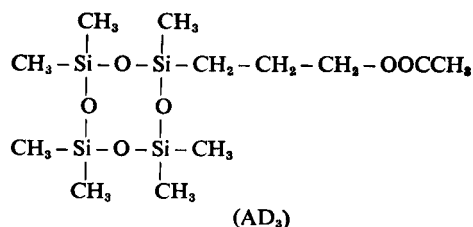
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ABSTRACT

Four γ -substituted-propylcyclotetrasiloxanes have been synthesized. Emulsion copolymerizations of these cyclosiloxanes with octamethylcyclotetrasiloxane have been carried out both in cationic and anionic emulsion systems. By way of these reactions, stable emulsions of organosilicon polymers which contain carbonfunctional groups such as γ -hydroxypropyl, γ -acetoxypropyl and γ -chloropropyl have been obtained.

The effects of temperature, catalyst and the amount of γ -substituted-propylcyclotetrasiloxanes in emulsion copolymerizations have been studied.

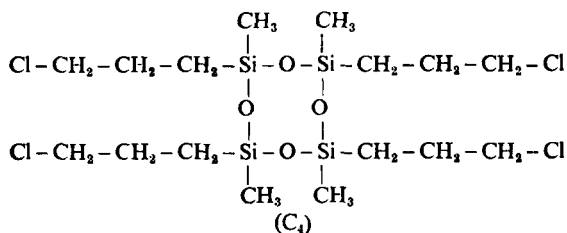
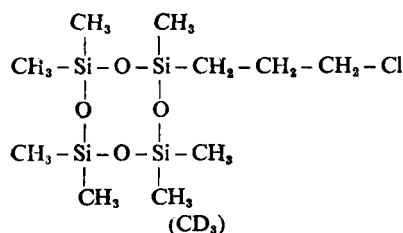
Emulsion polymerization of organosiloxanes is a new method developed in recent two decades for the synthesis of organosilicon polymers. It can be used to prepare stable emulsion of organopolysiloxanes having hydroxyl end groups. Previous works mainly concentrated on the emulsion polymerization of methylsilicon compounds and their applications^[1-3]. In order to study the emulsion polymerization of organosilicon compounds containing carbonfunctional groups, we have synthesized four γ -substituted-propylcyclotetrasiloxanes.



1-(γ -acetoxypropyl)-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (AD₃)

1-(γ -hydroxypropyl)-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (HD₃)

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1-(γ -chloropropyl)-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (CD_3)

1,3,5,7-tetra-(γ -chloropropyl)-1,3,5,7-tetramethylcyclotetrasiloxane (C_4)

D = $(\text{CH}_3)_2\text{SiO}$ unit

H = $\text{HOCH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)\text{SiO}$ unit

A = $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)\text{SiO}$ unit

C = $\text{ClCH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)\text{SiO}$ unit

Emulsion copolymerizations of the above-mentioned cyclosiloxanes with octamethylcyclotetrasiloxane have been carried out in both cationic and anionic emulsifier systems, and the stable emulsions of organosilicon polymers containing carbonfunctional groups such as γ -hydroxypropyl, γ -acetoxypropyl and γ -chloropropyl have been obtained. In this work we have studied the effects of various factors such as temperature, catalyst, emulsifier and the amount of γ -substituted-propylcyclotetrasiloxanes etc. on copolymerization by determining the percentage of monomer conversion and the change of molecular weight of polymers under different conditions.

EXPERIMENTAL

1. Synthesis of γ -substituted-propylcyclotetrasiloxanes

γ -hydroxypropyl-heptamethylcyclotetrasiloxane (HD_3): 258 g. (2.0 mol) dimethyldichlorosilane and 100 g. (0.5 mol) $(\text{CH}_3)_2\text{Si}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_2\text{CH}_3)_2$ ^[4] ($n_{\text{D}}^{20} = 1.4513$) were dissolved in 200 ml diethyl ether and then the solution was added dropwise with stirring to a mixture of 600 ml diethyl ether, 100 ml ethanol and 600 ml 1N hydrochloric acid. The flask was ice-cooled previously. After completion of the addition, stirring was continued for one hour. The ether layer was separated out and washed with water until it became neutral, then, dried over Na_2SO_4 and distilled to remove ether and D_4 . Under vacuum distillation, HD_3 32.5 g. (yield 19.1%) was obtained. The physical constants and elemental analytical data are listed in Table 1.

IR spectra: 3370 cm^{-1} (CH_2OH), $1465(\text{CH}_2)$, $1080\text{ cm}^{-1}(\text{SiOSi})$.

NMR spectra: (CCl_4): 0.5(2H, t, $\text{Si}-\text{CH}_3$), 1.5–1.75(2H, m, $\text{C}-\text{CH}_2-\text{C}$), 2.13 (1H, s, $-\text{OH}$), 3.58(2H, t, CH_2O).

γ -acetoxypropyl-heptamethylcyclotetrasiloxane (AD_3): The above experiment was repeated by using 258 g. (2.0 mol) dimethyldichlorosilane and $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)-\text{SiCl}_2$ 108 g. (0.5 mol). AD_3 67.6 g. (yield 35.3%) was obtained.

IR spectra: 1750 cm^{-1} ($\text{C}=\text{O}$), $1460\text{ cm}^{-1}(\text{CH})$, $1080\text{ cm}^{-1}(\text{SiOSi})$, $1260\text{ cm}^{-1}(\text{SiCH}_3)$.

NMR spectra (CCl_4): 0.45 (2H, t, SiCH_2), 1.35–1.7 (2H, m, $\text{C}-\text{CH}_2-\text{C}$), 1.88 (3H, s, $\text{C}-\text{CH}_3$), 3.92 (2H, t, CH_2O).

γ -chloropropyl-heptamethylcyclotetrasiloxane (CD_3): Equipments and operation were the same as above and 258 g. (2.0 mol) dimethyldichlorosilane and $ClCH_2CH_2CH_2(CH_3)-SiCl_2$ ^[4] ($n_D^{20} = 1.4586$) 96g. (0.5 mol) were used. CD_3 61.5 g. (yield 36.3%) was obtained.

IR spectra: $1465\text{ cm}^{-1}(CH_2)$, $1080\text{ cm}^{-1}(SiOSi)$, $1260\text{ cm}^{-1}(Si-CH_3)$.

NMR spectra: 0.53 (2H, t, $Si-CH_2$), 1.58–1.84 (2H, m, $C-CH_2-C$), 3.33 (2H, t, $-CH_2Cl$).

Tetra-(γ -chloropropyl)-tetramethylcyclotetrasiloxane (C_4): In the same way, 114 g. (0.6 mol) $ClCH_2CH_2CH_2(CH_3)SiCl_2$ ^[4] ($n_D^{20} = 1.4586$) in 100 ml diethyl ether was added dropwise to a mixture of 200 ml diethyl ether and 150 ml water. Finally under vacuum distillation gave C_4 27.5 g. (yield 36.3%).

IR spectra: $1465\text{ cm}^{-1}(CH_2)$, $1020\text{ cm}^{-1}(SiOSi)$, $1270\text{ cm}^{-1}(Si-CH_3)$.

Mass spectra: 546 (M^+), 531 ($M^+ - CH_3$).

Table 1 Physical constants and elemental analysis of γ -substituted-propylcyclotetrasiloxanes

Compound	Boiling point (°C)	n_D^{20}	d_4^{20}	Elemental analysis					
				C		H		Si	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
AD	102° / 2 mm	1.4175	1.0169	37.66	37.40	7.90	7.99	29.35	29.36
HD	104–106° / 1.5	1.4152	0.9969	35.26	34.84	8.28	8.15	32.97	32.90
CD	129–130° / 20	1.4217	1.0262	33.45	33.13	7.58	7.58	31.28	31.36
C	194° / 6	1.4632	1.1474	35.16	35.38	6.64	6.68	20.55	20.62

2. Emulsion copolymerization

The composition of emulsion copolymerization was: water (67–77%), monomer (20–30%), the number of γ -substituted propylcyclotetrasiloxane chain unit was 1–10% in the total number of siloxane chain unit, and dodecylbenzenesulfonic acid (DBSA, 0.1–0.25%) as emulsifier and catalyst in the anionic emulsion copolymerization, or dimethylbenzyl-dodecylammonium bromide (2–2.5%) as emulsifier and potassium hydroxide as catalyst in the cationic emulsion copolymerization.

Cationic Emulsion Copolymerization: Emulsifier, monomer and water were placed in a three-necked flask fitted with stirrer, thermometer and reflux condenser. After stirring at high speed for 20 minutes, the mixture was heated to the desired temperature. Then the catalyst was added and the reaction time recorded.

Anionic Emulsion Copolymerization: Emulsifier, monomer and water were placed in a three-necked flask fitted with stirrer, thermometer and reflux condenser. After stirring at high speed for 10 minutes, the flask was steeped into a water bath which had been previously heated to the desired temperature. Then the reaction time was recorded.

Determination of Monomer Conversion: The method was used according to Ref. [2].

Determination of Intrinsic Viscosity of Polymers: To 5 ml emulsion, equal volume of precipitating agent (95% C_2H_5OH + 4% H_2O + 1% KBr) was added to precipitate the

copolymer. Subsequently, the copolymer was dissolved in benzene and reprecipitated by methanol. The purified product was put in vacuum oven under 50°C / 20 mmHg for 8 hours to remove the solvent. Intrinsic viscosity of the polymer was determined by using Ubbelohde viscosimeter with benzene as solvent.

RESULTS AND DISCUSSION

1. The effect of reaction temperature

Cationic and anionic emulsion copolymerization were carried out at temperature ranging from room to 100°C . Experiments showed that for each increase of 10°C , the reaction rates approximately doubled.

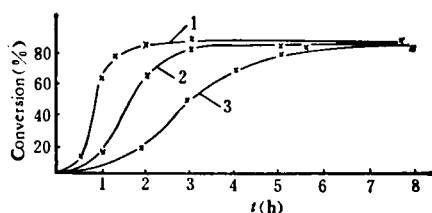


Fig. 1 Rate of monomer conversion in anionic emulsion copolymerization (1% H unit)
1— 80° ; 2— 70° ; 3— 60°

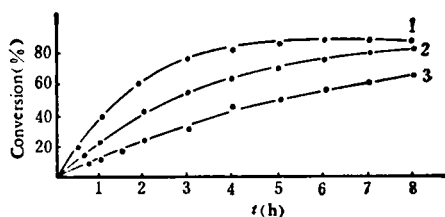


Fig. 2 Rate of monomer conversion in cationic emulsion copolymerization (1% A unit)
1— 80° ; 2— 70° ; 3— 60°

By the determination of intrinsic viscosity of copolymers which were produced in emulsion copolymerization under different temperature, we found that the higher the reaction temperature is, the faster the molecular weight increase at initial stage of reaction (see Fig. 3), but the lower the molecular weight under equilibrium (see Figs. 3 and 4).

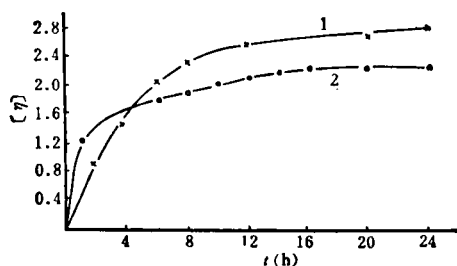


Fig. 3 Variation of intrinsic viscosity of copolymer during anionic emulsion copolymerization (5% C unit)
1— 60° ; 2— 80° .

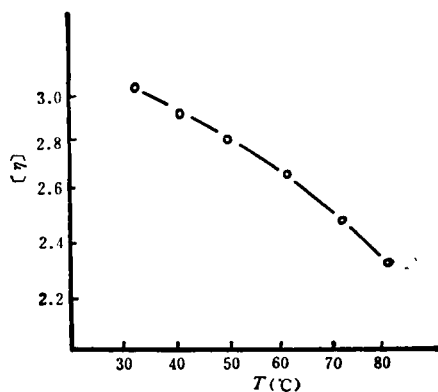


Fig. 4 Relationship between intrinsic viscosity of copolymer and reaction temperature (cationic emulsion system, 1% H unit)

In emulsion the molecular weight of copolymers under equilibrium changed reversibly with the temperature. The intrinsic viscosity $[\eta]$ of a copolymer containing 1% A unit obtained from a cationic emulsion reacted at 70°C for 48 hours was 2.60 when the emulsion

was laid up at room temperature for 30 days, $[\eta] = 3.99$; and then it was heated to 70°C again for 48 hours, and $[\eta] = 2.53$. It was postulated that in emulsion system there existed equilibrium between condensation and hydrolysis of polymers from beginning to end under the action of catalyst. The equilibrium point changes with reaction temperature.

2. The effect of the amount of γ -substituted-propylcyclotetrasiloxanes

In emulsion copolymerization, a small amount of γ -substituted-propylcyclotetrasiloxane could obviously affect reaction rate and percentage of monomer conversion. Fig. 5 showed that as the amount of γ -substituted-propylcyclotetrasiloxane increasing, the reaction rate increased at initial stage but decreased at later stage, and the percentage of monomer conversion reduced near the equilibrium.

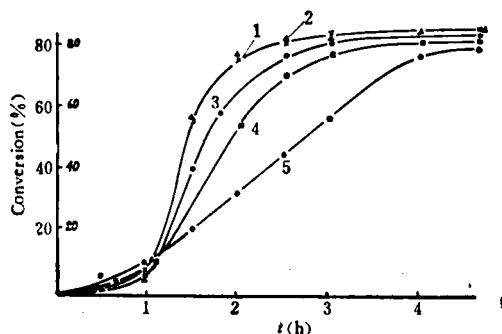


Fig. 5 Effect of the content of C unit on anionic emulsion copolymerization ($\text{CD}_3 + \text{D}_4$, 70°C)
 —x— pure D_4 ; — Δ — 1% C unit; —●— 3% C unit;
 —□— 5% C unit; —○— 10% C unit.

3 Effect of catalyst

In anionic emulsion copolymerization dodecylbenzensulfonic acid (DBSA) was used as both emulsifier and catalyst. In general its amount was 1–5% of the monomer. Experiments showed that the reaction rate depended upon the molar ratio between catalyst and siloxane unit (see Fig. 7), regardless of the amount of water used (see Fig. 6).

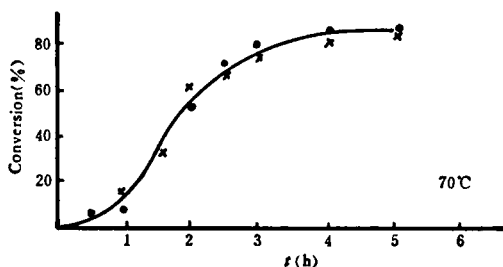


Fig. 6 Effect of amount of water used on reaction rate (1% H unit, 70°C)

Weight ratio between DBSA and monomers	Concentration of DBSA in water	Content of monomer in emulsion
—x— 0.017	0.71%	30%
—●— 0.017	0.36%	17.7%

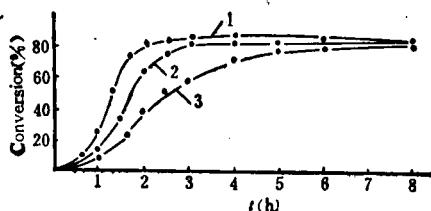


Fig. 7 Effect of amount of DBSA on anionic emulsion copolymerization (1% H unit, 70°C)
Weight ratio between DBSA and monomers
1—5%; 2—2.5%; 3—1.25%.

In the cationic emulsion copolymerization of γ -acetoxypropyl-heptamethylcyclotetra-siloxane (AD_3) and D_4 , KOH was used both as catalyst for ring-opening polymerization and saponifying agent for acetoxy group in AD_3 . The final polymer obtained was γ -hydroxypropyl-methylpolysiloxane.

4. Relationship between percentage of monomer conversion and molecular weight of polymer

From Figs. 8 and 9, we find that the polymerization process may be divided into two stages. In the first stage, the conversion increases rapidly while the molecular weight increases rather slowly. When the percentage of monomer conversion exceeds 70%, the conversion rate slows down gradually, but the molecular weight continues to increase until it reaches equilibrium. It is considered that at the first stage the ring-opening reaction was the main reaction, and at later stage the condensation of the oligomers formed previously predominates.

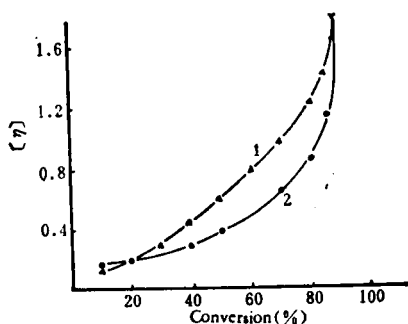


Fig. 8 Relationship between monomers conversion and intrinsic viscosity in cationic emulsion copolymerization (1% A unit)
1—80°; 2—60°.

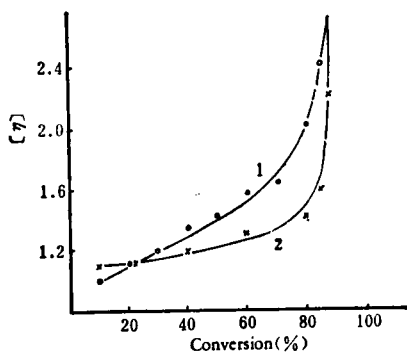


Fig. 9 Relationship between monomers conversion and intrinsic viscosity in anionic emulsion copolymerization (1% C unit)
1—80°; 2—60°.

5. Chemical properties of some of the copolymers

GPC studies of polymers obtained from copolymerization of CD_3 with D_4 or HD_3 with D_4 showed that there was only one peak appeared in the spectrogram. It represented the copolymer alone.

The emulsion and benzene solution of γ -hydroxypropylmethylpolysiloxane were stable. But if there was no solvent or water present, the polymer would be unstable. If it were laid up at room temperature for several days, cross-linking would occur. Moreover, γ -hydroxy-propyl-methylpolysiloxane could react with some compounds also (see Table 2).

Table 2 Chemical reactions of γ -hydroxypropyl-methylpolysiloxane

Polymer	Reactant	Condition	Result
Polysiloxane containing 1% H unit	Dimethyldichlorosilane	Mixing at room temperature	Cross linked in a twinkling
	Tolylenediisocyanate	Mixing at room temperature	Cross linked in a twinkling
	Pyromellitic anhydride	Mixing and heating	Solidify
	Cyclosilazane	Mixing and heating	Solidify

γ -chloropropyl-methylpolysiloxane could react with tertiary amine to form quaternary ammonium compounds after polysiloxane containing 10% C unit dissolved in xylene was refluxed with pyridine for 48 hours, white precipitate (AgCl) was formed on an addition of water solution of AgNO_3 . In the IR spectra of the product, there appeared characteristic peaks of pyridinium ring at 1500 cm^{-1} and 1650 cm^{-1} .

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